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Titanium-Catalyzed Rearrangement and Olefin-Exchange of Grignard Reagents[1]

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In the presence of small amounts of titanium tetrachloride, isopropylmagnesium bromide rearranges to *n*-propylmagnesium bromide. The rearrangement was demonstrated by the formation of 1-deuteropropane when titanium tetrachloride was added to isopropylmagnesium bromide and the mixture then decomposed with deuterium oxide, and by the formation of *n*-butyl alcohol on reaction of the mixture with formaldehyde. Titanium tetrachloride also catalyzes an exchange between alkylmagnesium halides and terminal olefins, yielding the Grignard reagent derived from the added olefin: $RCH{=}CH_2 + C_3H_7MgBr \xrightarrow{TiCl_4} C_3H_6 + RCH_2CH_2MgBr$. This exchange provides a one-step method for preparing Grignard reagents from olefins. A 45% yield of 1-hexanol was obtained when *n*-propylmagnesium bromide, 1-pentene, and titanium tetrachloride (mole ratio 1:1:0.03) were refluxed for sixteen hours in diethyl ether and then allowed to react with formaldehyde. Both rearrangement and olefin-exchange may be explained by a mechanism involving elimination of Ti—H from an intermediate alkyltitanium compound followed by addition of the titanium hydride to the olefin.

George and Ladd[2] have reported that when alkylmagnesium halides react with chlorosilanes in the presence of a trace of titanium tetrachloride much of the Si—Cl is converted to Si—H. Coupling of the chlorosilane with the Grignard reagent also occurs, but when isopropylmagnesium bromide is used the coupled product contains both *n*-propyl and isopropyl groups:

$$(CH_3)_2CHMgBr + ClSi\equiv \xrightarrow{TiCl_4} (CH_3)_2CHSi\equiv + CH_3CH_2CH_2Si\equiv \quad (1)$$

George and Ladd did not establish whether formation of rearranged products occurred only in reactions with silicon compounds or whether the Grignard reagent isomerized prior to reaction:

$$(CH_3)_2CHMgBr \xrightarrow{TiCl_4} CH_3CH_2CH_2MgBr \quad (2)$$

No such rearrangement of alkylmagnesium compounds has been reported, and in view of the frequency with which Grignard reactions are used as proof of structure, it appeared to be of importance to clarify this point. The initial object of the present investigation was to find out if rearrangement 2 occurred and if so to determine, if possible, the mechanism of the reaction.

Isomerization of Propylmagnesium Bromides.—The reaction chosen for studying the rearrangement of the propylmagnesium bromides was decomposition of the Grignard reagent with deuterium oxide. In addition to being rapid and free of side reactions it has the advantage that the mixture of deuteropropanes can be easily analyzed by infrared spectrophotometry. Furthermore, it is known to proceed without rearrangement; *n*-propylmagnesium bromide yields only 1-deuteropropane and isopropylmagnesium bromide only 2-deuteropropane.[3]

Small amounts of titanium tetrachloride (2×10^{-4} -10^{-2} mole) were added at 0° to a Grignard reagent prepared from 0.1 mole of magnesium and 0.11 mole of propyl bromide and, after a suitable interval, deuterium oxide was added and the C_3 hydrocarbons were collected and analyzed. There was

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[1] Presented in part at the 140th Meeting of the American Chemical Society, Chicago, Ill., September, 1961.

[2] P. D. George and J. R. Ladd, paper presented at the 140th Meeting of the American Chemical Society, Chicago, Ill., September, 1961.

[3] H. L. McMurry, V. Thornton, and F. E. Condon, *J. Chem. Phys.*, **17**, 918 (1949). There is some indication that a very small amount of rearrangement occurs in reaction of isopropylmagnesium bromide with deuterium oxide in butyl ether [J. Turkevich, E. Solomon, and F. M. Wrightson, *J. Am. Chem. Soc.*, **70**, 2638 (1948)].

TABLE I

ISOMERIZATION OF ISOPROPYLMAGNESIUM BROMIDE[a]

No.	$TiCl_4$ (Moles)	Time (Hr. at 0°)	$\frac{CH_3CH_2CH_2D}{TiCl_4}$	$\frac{CH_3CH_2CH_2D}{(CH_3)_2CHD}$
1	0	1.25	0	0
2	2.2×10^{-3}	0[b]	6.5	.267
3	2.2×10^{-3}	1.25	7.4	.321
4	2.2×10^{-3}	1.25	6.5	.270
5	2.2×10^{-3}	5.0	7.6	.351
6	2.2×10^{-4}	1.25	21.0	.065
7	4.4×10^{-3}	1.25	4.6	.609
8	10^{-2}	1.25	2.5	2.1
9	2.2×10^{-3}	1.25 (reflux)	6.7	0.200
10	3.3×10^{-3}	1.25	..	0

[a] Prepared from 0.1 mole isopropyl bromide and 0.1 mole magnesium in 30 ml. of diethyl ether. [b] Addition of deuterium oxide started immediately after addition of titanium tetrachloride.

no detectable rearrangement of either isopropyl or *n*-propylmagnesium bromide in the absence of titanium tetrachloride and no rearrangement was observed when the *n*-propylmagnesium bromide was treated with titanium tetrachloride. In all experiments where titanium tetrachloride was added to isopropylmagnesium bromide, however, significant amounts of 1-deuteropropane were produced on reaction with deuterium oxide. This appears to be conclusive proof that rearrangement of the Grignard reagent occurred prior to reaction. The possibility that 1-deuteropropane might be formed by isomerization of 2-deuteropropane by the alkylmagnesium bromide–titanium tetrachloride complex was eliminated by adding 2-deuteropropane to a mixture of *n*-amylmagnesium bromide and titanium tetrachloride. When this mixture was decomposed with deuterium oxide in the usual manner the recovered C_3 hydrocarbon contained only 2-deuteropropane.

The effect of varying titanium tetrachloride concentration and reaction time on the products of reaction of isopropylmagnesium bromide with deuterium oxide are listed in Table I. The recovery of C_3 hydrocarbons (propane, propylene, and the monodeuteropropanes) ranged from 75–95%. The discrepancy is partly due to the formation of small amounts of C_6 hydrocarbons, principally 2,3-dimethylbutane. A more important cause is the fact that formation of the Grignard reagent was never quantitative; some unchanged magnesium was always present. In addition, no attempt was made to achieve a quantitative separation of the C_3 hydrocarbons from the ether; the object instead was to be sure that the sample consisted only of C_3 hydrocarbons. With the procedure used, reproducibility was poor (compare experiments 3 and 4). A solid complex forms immediately upon addition of the titanium tetrachloride, and results are undoubtedly influenced by the exact conditions (efficiency of agitation, etc.) under which the titanium tetrachloride is added. This lack of reproducibility renders interpretation somewhat difficult, but it appears that the ratio of 1-deuteropropane to 2-deuteropropane is affected only slightly by increase in reaction time (experiments 2, 3, 4, and 5), but is very much dependent on the ratio of Grignard reagent to titanium tetrachloride; the ratio of 1D/2D increased from 0.065 to 2.1 as the ratio of titanium tetrachloride to isopropylmagnesium bromide was increased from 1:400 to 1:10 (experiments 3, 4, 6, 7, and 8). Propane and propylene also increased at higher titanium tetrachloride concentrations, so that the greater 1D/2D ratio was only partly due to an increase in the amount of 1-deuteropropane. At the highest titanium tetrachloride level used, the deuteropropanes made up only 48% of the C_3 hydrocarbons. Propane and propylene are always produced in the preparation of isopropylmagnesium bromide,[3,4] but in this case much of it probably comes from the disproportionation of propyl radicals arising from the decomposition of an intermediate organotitanium compound.[5,6] The C_3 hydrocarbons were not collected separately during the various stages of the reaction, so that they contain material formed in preparation of the Grignard reagent and during the reaction with titanium tetrachloride, as well as that produced on reaction with deuterium oxide. In all cases, however, the amount of 1-deuteropropane produced was much greater than the amount of titanium tetrachloride added, ranging from 2.5 to 20 moles per mole of titanium tetrachloride. The ratio of 1-deuteropropane to titanium tetrachloride was greatest at low titanium tetrachloride concentrations.

Mechanism.—A plausible mechanism for the rearrangement is suggested by that established by Brown for the rearrangement of alkylboron compounds. Secondary and tertiary alkylboranes re-

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[4] C. D. Wagner and D. P. Stevenson, *J. Am. Chem. Soc.*, **72**, 5785 (1950).

[5] D. F. Herman and F. E. Nelson, *J. Am. Chem. Soc.*, **75**, 3877, 3882 (1953).

[6] A small amount of the propane comes from reaction of the Grignard reagent with water adsorbed on the glass surface of the reaction vessel and that introduced (as hydrogen chloride) with the titanium tetrachloride.

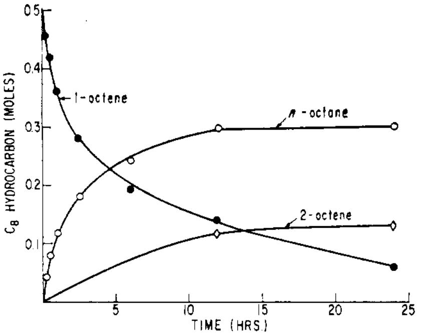

Fig. 1.—Products from exchange of 0.5 mole of 1-octene with *n*-propylmagnesium bromide

arrange by a series of eliminations and readditions to the primary isomers[7]:

$$CH_3CH_2CH(BR_2)CH_3 \longrightarrow CH_3CH_2CH{=}CH_2 + BR_2H \quad \big\downarrow\!\uparrow \quad CH_3CH_2CH_2CH_2BR_2 \qquad (3)$$

An analogous reaction sequence for the titanium-catalyzed rearrangement of Grignard reagents may be written. In the first step the Grignard reagent reacts to form an organotitanium compound,[5] followed by elimination of the elements of TiH (shown here for convenience as $TiHCl_3$, but probably present as part of the solid Ziegler-type complex), and readdition terminally to the olefin produced in the second step:

$$(CH_3)_2CHMgBr + TiCl_4 \longrightarrow (CH_3)_2CHTiCl_3 + MgBrCl \qquad (4)$$

$$(CH_3)_2CHTiCl_3 \longrightarrow TiHCl_3 + CH_3CH{=}CH_2 \qquad (5)$$

$$TiHCl_3 + CH_3CH{=}CH_2 \rightleftarrows CH_3CH_2CH_2TiCl_3 \qquad (6)$$

From the electronegativities of the atoms involved[8] it would be expected that the titanium-hydrogen bond would be strongly polarized in the direction $Ti^+—H^-$, so that addition of the titanium to the terminal atom of propylene would be expected on electronic grounds as in the case of the addition of boron hydrides.[9] Steric considerations might also be important, particularly if the reaction occurs on a solid surface. The fact that each mole of titanium tetrachloride produces several moles of rearranged product requires that the alkyltitanium compound can exchange with the organomagnesium compound (principally isopropylmagnesium bromide, at least in the early stages):

$$CH_3CH_2CH_2TiCl_3 + RMgBr \rightleftarrows CH_3CH_2CH_2MgBr + RTiCl_3 \qquad (7)$$

Inasmuch as this mechanism implies that the Grignard reagent isomerizes before reaction with the substrate it would be expected that the formation of rearranged products should not be confined to reaction with chlorosilanes but should be observed in all reactions of the Grignard reagent which are carried out in the presence of titanium tetrachloride. This prediction was confirmed when formaldehyde was added to a mixture of 0.1 mole isopropylmagnesium bromide and 0.002 mole of titanium tetrachloride. A 47% yield of butyl alcohol was obtained, of which 81% was isobutyl alcohol and 19% *n*-butyl alcohol.

It also suggests that if an olefin other than that derived from the original alkyl group were present it should compete for the Ti—H in (6):

$$RCH{=}CH_2 + TiHCl_3 \longrightarrow RCH_2CH_2TiCl_3 \qquad (8)$$

If the added olefin is less volatile (or more reactive) than propylene, it should be possible to convert it to the Grignard reagent by reaction with propylmagnesium bromide in the presence of titanium tetrachloride:

$$C_3H_7MgBr + RCH{=}CH_2 \xrightarrow{TiCl_4} CH_3CH{=}CH_2 + RCH_2CH_2MgBr \qquad (9)$$

This possibility was tested by adding one equivalent of 1-pentene to a mixture of isopropylmagnesium bromide and titanium tetrachloride (mole ratio 40:1) and refluxing overnight. Hydrolysis of the mixture produced a 36% yield of *n*-pentane, indicating that exchange (9) had occurred.[10] Small amounts of *cis*- and *trans*-2-pentene were also formed. A similar experiment with *n*-propylmagnesium bromide gave a 46% yield of *n*-pentane. A further demonstration of exchange (9) was provided by heating 1-pentene with the alkylmagnesium bromide–titanium tetrachloride mixture and then adding formaldehyde. A 45% yield of 1-hexanol was obtained with *n*-propylmagnesium bromide and smaller amounts were obtained with ethylmagnesium bromide and isopropylmagnesium bromide. No exchange could be detected when the Grignard reagent was methylmagnesium bromide. The requirement for a beta hydrogen in the Grignard reagent is consistent with the elimination-addition sequence suggested above, but does not exclude other mechanisms. The combination of a Grignard reagent with titanium tetrachloride belongs to the class of "Ziegler" catalysts[11,12] and the olefin exchange reaction corresponds in many ways to chain termination by transfer to monomer in a Ziegler polymerization, for which a number of mech-

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[7] H. C. Brown and B. L. Subba Rao, *J. Org. Chem.*, **22**, 1136 (1957); *J. Am. Chem. Soc.*, **81**, 6434 (1959).

[8] L. Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell University Press, Ithaca, New York, 1945, p. 93.

[9] H. C. Brown, *Tetrahedron*, **12**, 117 (1961).

(10) The possibility of such an exchange had previously been indicated by an observation of George and Ladd (ref. 2). They obtained a small yield of hexyldiethylsilane from the reaction of isopropylmagnesium bromide and 1-hexene with diethyldichlorosilane containing titanium tetrachloride. This could have arisen, however, from the addition of Si—H to the olefin, a reaction which occurs readily in the presence of suitable metal catalysts (C. Eaborn, "Organosilicon Compounds," Academic Press, Inc., New York, N. Y., 1960, p. 194).

(11) K. Ziegler, Belgian Patent 534,888 (1955).

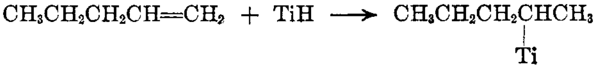
(12) P. E. M. Allen and J. F. Harrod, *Makromol. Chem.*, **32**, 153 (1959).

anisms have been proposed.[13] The scheme outlined above is preferred only for its simplicity; it accounts satisfactorily for most of the observed facts[14] and has been useful in predicting new reactions. Whatever the mechanism, a process by which an olefin is converted in one step to a Grignard reagent should have preparative value. The application of this exchange in organic synthesis is being investigated and will be reported separately.[15]

Isomerization of Olefins during Exchange.—Although the data in Table I suggest that at a constant catalyst concentration the extent of rearrangement of isopropylmagnesium bromide at 0° is almost independent of reaction time, the olefin-exchange reaction (9) is definitely time dependent. A mixture of 1-octene, *n*-propylmagnesium bromide, and titanium tetrachloride (mole ratio 1:1:0.03) was refluxed in ether. Aliquots were removed periodically, decomposed with dilute acid, and analyzed for octane and octene by gas chromatography. The concentration of octane increased continuously over the first twelve hours, at which time it had reached 60% of the amount corresponding to complete exchange. There was no further change in octane during the next twelve hours, although the 1-octene continued to decrease. Two other compounds, identified as *cis*- and *trans*-2-octene, increased slowly throughout the reaction until at the end of twenty-four hours the concentrations of 1- and 2-octene were approximately equal.

The absence of an appreciable time dependence in the rearrangement of isopropylmagnesium bromide at 0° suggests that the rearrangement may not proceed by the same mechanism as the olefin-exchange reaction, but this point cannot be decided from the information available at present. The conversion of the isopropyl to the *n*-propyl Grignard reagent can be made almost complete by carrying out the reaction at a higher temperature under propylene. When a mixture of isopropylmagnesium bromide and titanium tetrachloride was shaken for twenty hours at room temperature under 10 p.s.i.g. of propylene and then decomposed with deuterium oxide, the ratio of rearranged to unrearranged deuteropropane was 4.93, compared with a ratio of approximately 0.3 in the reactions carried out at the same catalyst level at 0°.

Internal olefins do not undergo the exchange reaction with *n*-propylmagnesium bromide under the conditions used in this work (16–20 hours reflux in ether, 0.03 mole of titanium tetrachloride per mole of Grignard reagent). No cyclohexanecarboxylic acid could be detected on carbonation of the product from cyclohexene. Reaction of formaldehyde with the product obtained from 2-pentene (85% *cis*, 15% *trans*) yielded neither 2-ethyl-1-butanol nor 2-methyl-1-pentanol. This inertness of the internal olefins provides a simple explanation for the formation of 2-pentene and 2-octene in the reaction of 1-pentene and 1-octene with the Grignard reagent–titanium tetrachloride mixture. Although the reaction of TiH with the 1-pentene appears to yield predominantly the terminal alkyltitanium compound, it would be surprising if a small amount of the reverse addition did not occur as well:



$$CH_3CH_2CH_2CH{=}CH_2 + TiH \longrightarrow CH_3CH_2CH_2\underset{\displaystyle Ti}{\underset{|}{C}}HCH_3$$

The secondary alkyltitanium compound can then eliminate according to the suggested mechanism to yield either 1-pentene or 2-pentene. The 1-pentene may again add TiH, while 2-pentene, being unreactive, continues to build up in the reaction mixture and may eventually be present in substantial amounts.

Experimental

Materials.—The propyl bromides used were commercially available materials, redistilled, and shown by gas phase chromatography to be essentially free of isomers. Deuterium oxide was used as purchased from Stuart Oxygen Co. and was 99.55% D. All other materials were standard analytical grade research items used without further purification.

Reaction of Propylmagnesium Bromide–Titanium Tetrachloride Mixtures with Deuterium Oxide.—A solution of 13.5 g. (0.11 mole) of the propyl bromide in 10 ml. of diethyl ether was slowly added to 2.43 g. (0.1 g.-atom) of magnesium in 20 ml. of ether over a period of *ca.* 30 min. in a small flask equipped with a stirrer, dropping funnels, and a reflux condenser which was connected to a Dry Ice trap protected by a nitrogen bypass. The mixture was then cooled in ice and titanium tetrachloride was added from a hypodermic syringe. A brown solid was formed immediately on addition of the titanium tetrachloride. The mixture was stirred for the desired time and 5 ml. of deuterium oxide was slowly added. After addition was complete the mixture was allowed to warm to room temperature and was then heated under reflux for a few minutes. The Dry Ice trap containing the deuteropropanes and the by-product propane and propylene, along with a considerable amount of ether, was attached to a high vacuum line and the C_3 hydrocarbons were separated from the ether by repeated transfers at −78°. The C_3 fraction was transferred to a calibrated bulb, allowed to vaporize, and the amount determined by measurement of the pressure. An infrared cell (10-cm. path) was filled to a pressure of 600–700 mm. for analysis.

Analysis of Deuteropropanes.—The C_3 hydrocarbons were analyzed for propane, propylene, 1-deuteropropane, and 2-deuteropropane. The bands used were for propane 746.5 cm.$^{-1}$; for propylene 988 cm.$^{-1}$; for 1-deuteropropane 698 cm.$^{-1}$, 742.5 cm.$^{-1}$, and 1285 cm.$^{-1}$; for 2-deuteropropane 663 cm.$^{-1}$. The spectra contained no bands other than those due to these compounds. The propane and propylene used in constructing the calibration curves were Phillips

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(13) G. Natta, *J. Polymer Sci.*, **34**, 21 (1959); M. L. Cooper and J. B. Rose, *J. Chem. Soc.*, 795 (1959); P. Cossee, *Tetrahedron Letters*, No. 17, 12 (1960) and references cited therein.

(14) The formation of silicon hydrides in the reactions of chlorosilanes described by George and Ladd may be explained by the reaction:

$$TiH + SiCl \longrightarrow TiCl + SiH$$

This particular reaction has not been reported, but the conversion of chlorosilanes to silicon hydrides by other metal hydrides is well known. George and Ladd found that no reduction of chlorosilanes took place when the Grignard reagent was phenylmagnesium bromide, in agreement with the suggested TiH-elimination mechanism.

(15) Some preliminary results of this investigation have been reported [H. L. Finkbeiner and G. D. Cooper, *J. Org. Chem.*, **26**, 4779 (1961)].

Petroleum Co. Research Grade materials. Pure 1-deuteropropane and 2-deuteropropane for standards were prepared by the procedure of McMurry.[3]

Hydrolysis of Amylmagnesium Bromide–Titanium Tetrachloride Mixture in Presence of 2-Deuteropropane.—A Grignard reagent was prepared from 0.1 g.-atom of magnesium and 0.1 mole of *n*-amyl bromide. After the addition of 2.2×10^{-3} mole of titanium tetrachloride the mixture was cooled to −45° and 0.1 mole of pure 2-deuteropropane was introduced. The mixture was stirred for 1 hr. and then allowed to warm to 0°. The Dry Ice trap was changed and 5 ml. of deuterium oxide was added in the usual manner. The infrared spectrum of the C_3 hydrocarbon evolved during hydrolysis was identical with that of pure 2-deuteropropane.

Reaction of Formaldehyde with the Rearranged Grignard Reagent.—To a Grignard reagent prepared from 0.25 g.-atom of magnesium and 0.25 mole of isopropyl bromide in 100 ml. of diethyl ether was added at 0°, 5.5×10^{-3} moles of titanium tetrachloride. This reaction mixture was stirred for 1.25 hr. and then 10.20 g. (0.34 mole) of paraformaldehyde was depolymerized at 190–200° and carried into the ice-cooled reaction mixture with a nitrogen stream according to the method of Noller and Adams.[16] After the addition was complete the reaction mixture was warmed to room temperature and stirred for an additional 2 hr. The product was then hydrolyzed by adding 15 g. of ammonium chloride in 40 ml. of water and stirring for 1 hr. The ether solution was filtered off and the solid residue washed twice with 50-ml. portions of ether. The ether fractions were combined, dried over magnesium sulfate, and distilled through a 12-in. column packed with glass helices. A 10.5-g. fraction boiling from 90–125° was analyzed by gas chromatography. This showed isobutyl alcohol 7.18 g. (38.8%) and *n*-butyl alcohol 1.69 g. (9.2%), or a normal/iso ratio of 0.24.

Titanium Tetrachloride-Catalyzed Exchange of 1-Pentene.—A Grignard reagent was prepared from 0.1 mole of *n*-propyl bromide and 0.1 g.-atom of magnesium in 50 ml. of diethyl ether. The solution was cooled to 0° and 7.0 g. of 1-pentene was added, followed by 0.11 ml. (2.2×10^{-3} mole) of titanium tetrachloride. The mixture was refluxed for 18 hr., hydrolyzed by the addition of a saturated solution of ammonium chloride, and the organic layer was separated and analyzed by gas chromatography. The product contained 2.14 g. (30.6%) of recovered 1-pentene, 3.32 g. (46.1%) of *n*-pentane, and 1.25 g. (18%) of *cis*- and *trans*-2-pentene. A sample of the fraction assumed to be *n*-pentane was trapped and its identity was confirmed by its cracking pattern in a mass spectrometer. The other compounds were identified by their retention times and infrared spectra.

A similar experiment using isopropylmagnesium bromide yielded 1.79 g. (25.6%) of 1-pentene, 2.60 g. (36.2%) of *n*-pentane, and 0.76 g. (11%) of 2-pentene.

Exchange of 1-Octene.—To a Grignard reagent prepared from 0.5 mole of *n*-propyl bromide and 0.55 g.-atom of magnesium in 200 ml. of diethyl ether was added 56 g. (0.5 mole) of 1-octene and enough ether to bring the total volume to 400 ml. The solution was cooled to 0°, 1.4 ml. (0.0126 mole) of titanium tetrachloride was added, the mixture was refluxed, and 25-ml. samples were withdrawn at intervals, then decomposed with ice and dilute hydrochloric acid. The organic phase was separated and analyzed by gas chromatography, using *n*-heptane as the internal standard. Results are shown in Fig. 1.

Exchange of 1-Pentene with Grignard Reagents and Reaction with Formaldehyde. (I) ***n*-Propylmagnesium Bromide.**—A Grignard reagent prepared from 0.5 mole of *n*-propyl bromide and 0.55 g.-atom of magnesium in 200 ml. of ether was cooled to 0° and 35 g. (0.5 mole) of 1-pentene was added, followed by 1.5 ml. (0.014 mole) of titanium tetrachloride. The mixture was refluxed for 18 hr., cooled to room temperature, and allowed to react with formaldehyde generated by the pyrolysis of 25 g. of paraformaldehyde. The mixture was poured over ice, acidified with sulfuric acid, and distilled with steam. Fractional distillation of the organic layer yielded 20.74 g. (41%) of 1-hexanol, b.p. 96–98°/85 mm., $n^{20}\mathrm{D}$ 1.4185; reported b.p. 100°/90 mm.,[17] $n^{20}\mathrm{D}$ 1.4182.[18] Analysis by gas chromatography indicated that it was more than 98% pure. A second fraction of 4.0 g. had b.p. 98–101°/85 mm., $n^{20}\mathrm{D}$ 1.4193 and was more than 90% 1-hexanol. No 2-methyl-1-pentanol was detected.

(II) **Ethylmagnesium Bromide.**—The Grignard reagent was prepared from 0.5 mole of ethyl bromide and 0.55 g.-atom of magnesium in 200 ml. of ether and allowed to react with 1-pentene, titanium tetrachloride, and formaldehyde as in the example above. Distillation yielded 5.5 g. (11%) of 1-hexanol, b.p. 98°/86 mm., $n^{20}\mathrm{D}$ 1.4179. The largest single product was *n*-propyl alcohol, obtained in 42% yield.

(III) **Methylmagnesium Bromide.**—The reaction was carried out as in the preceding examples, using a Grignard reagent prepared from reaction of methyl bromide with 0.5 mole of magnesium in 200 ml. of diethyl ether. After steam distillation most of the ether was distilled and the small residue was analyzed by gas chromatography. The major component was ethanol; no 1-hexanol could be detected.

(IV) **Isopropylmagnesium Bromide.**—The reaction was carried out as in the preceding examples, using 0.1 mole of isopropyl bromide and with all other reagents proportionately reduced. The product was decomposed with 20% ammonium chloride and the steam distillation step was omitted. Distillation yielded a fraction of 1.91 g. (18%), b.p. 95–100°/85 mm., which was shown by gas chromatography to be approximately 90% 1-hexanol, along with small amounts of isobutyl alcohol, *n*-butyl alcohol, 1-pentanol, and higher boiling materials. A high-boiling residue of 4.5 g. apparently contained large amounts of the formal of 1-hexanol; 1-hexanol was obtained when this was refluxed overnight with 20% sulfuric acid.

Attempted Exchange of 2-Pentene.—A Grignard reagent was prepared from 0.5 mole of *n*-propyl bromide and 0.55 g.-atom of magnesium in 300 ml. of diethyl ether, 35 g. (0.5 mole) of 2-pentene (85% *cis*, 15% *trans*) was added and the solution was cooled to 0°. Titanium tetrachloride (1.40 ml., 0.013 mole) was added and the mixture was refluxed for 16 hr., and treated with formaldehyde as in previous examples. Distillation yielded 18 g. (48%) of *n*-butyl alcohol, b.p. 115–120°. Gas chromatography of the product and of the still residue showed no peaks corresponding to 2-ethyl-1-butanol or 2-methyl-1-pentanol.

Attempted Exchange of Cyclohexene.—A Grignard reagent was prepared from 0.5 mole of *n*-propyl bromide and 0.55 g.-atom of magnesium in 300 ml. of ether, 41 g. (0.5 mole) of cyclohexene and 1.40 ml. (0.013 mole) of titanium tetrachloride were added, and the mixture was refluxed for 18 hr. Dry gaseous carbon dioxide was added at −5° until there was no increase in temperature on increasing the flow rate. The mixture was decomposed with ice and sulfuric acid, and the ether extract was distilled, yielding 22.1 g. (50%) of butyric acid as the major product. No cyclohexanecarboxylic acid was detected on analysis of this fraction or of the still residue by gas chromatography.

Acknowledgment.—The authors are indebted to Miss Cynthia Lape for assistance in the experimental work.

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[16] C. R. Noller and R. Adams, *J. Am. Chem. Soc.*, **48**, 1085 (1926).

[17] L. M. Ellis, Jr., and E. E. Reid, *J. Am. Chem. Soc.*, **54**, 1674 (1932).

[18] A. I. Vogel, *J. Chem. Soc.*, 1814 (1948).